Electronic Supporting Information (ESI) for Dalton Transactions

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Influence of the substituent on the phosphine ligand in novel rhenium (I) aldehydes. Synthesis, computational studies and first insights into antiproliferative activity

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Index

Experimental Section:

1. Synthesis and characterization of novel rhenium (I) dicarbonyl phosphine aldehydes.

    a) NMR Spectrum of **2a-2c** compounds.
    b) Electrochemical studies
    c) Computational studies of rhenium (I) derivatives.

2. Cytotoxic studies of the new compounds in two cancer cell lines: HT-29 and PT-45.

1. Novel Rhenium dicarbonyl phosphine aldehydes [(η^5-C_5H_4CHO)Re(CO)$_2$PR$_3$].

a) NMR Spectra

a.1. Synthesis of [(η^5-C_5H_4CHO)Re(CO)$_2$PMe$_3$] (2a)

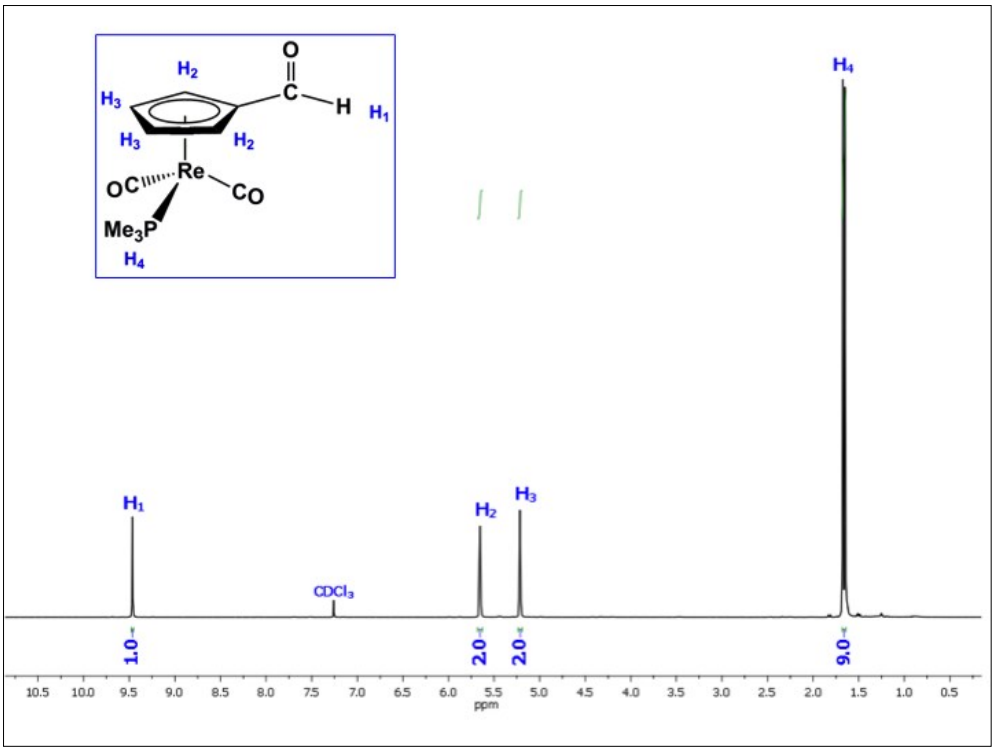

Figure S1. ^{1}H-NMR spectra (400 MHz) of a solution of **2a** (40 mM) in $CDCl_3$ at 298 K.

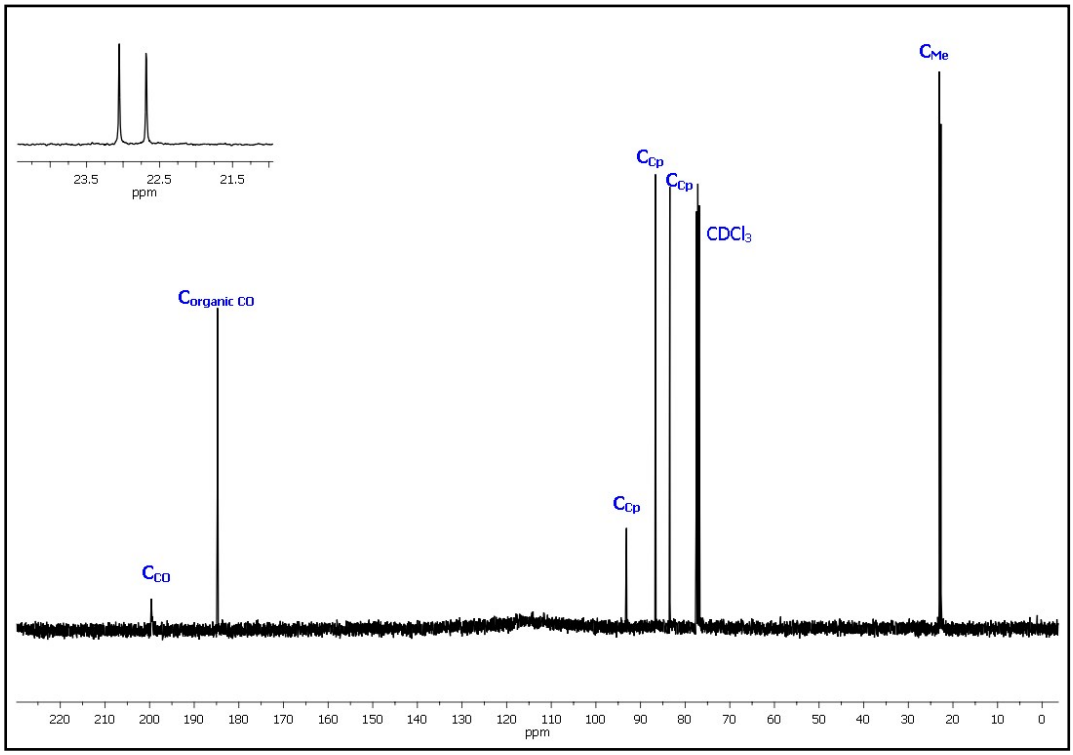

Figure S2. ^{13}C-NMR spectra (400 MHz) of a solution of **2a** (80 mM) in $CDCl_3$ at 298 K.

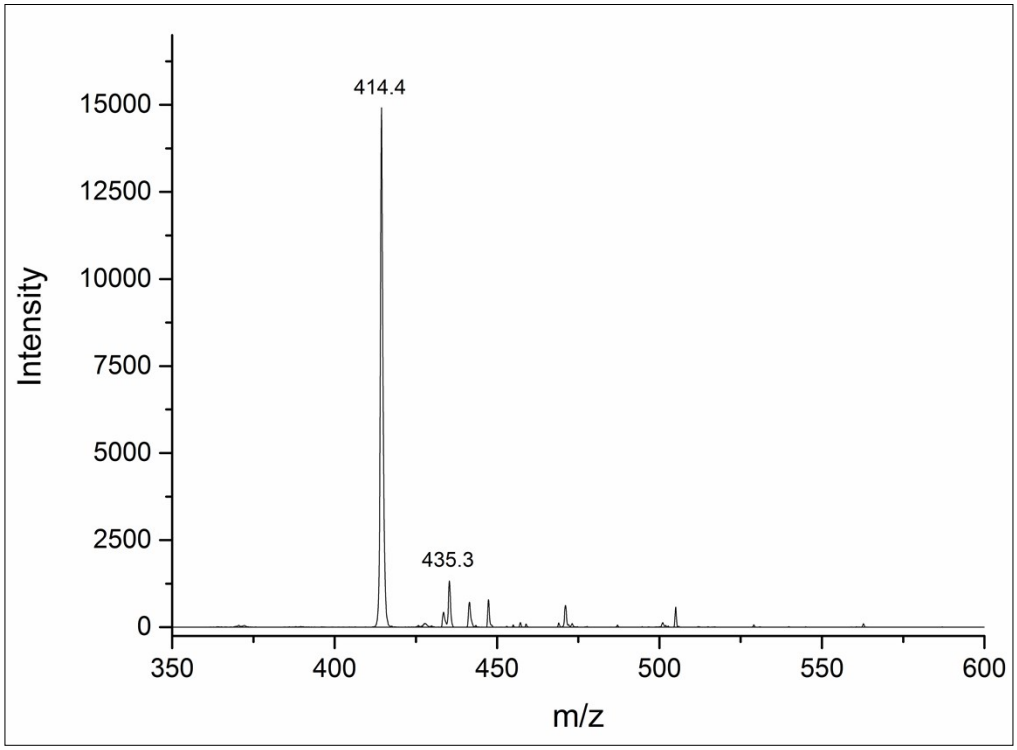

Figure S3. ESI-MS in CH_3CN of **2a** (1mg/ml).

a.2. Synthesis of $[(\eta^5\text{-}C_5H_4CHO)Re(CO)_2PPh_3]$ (2b)

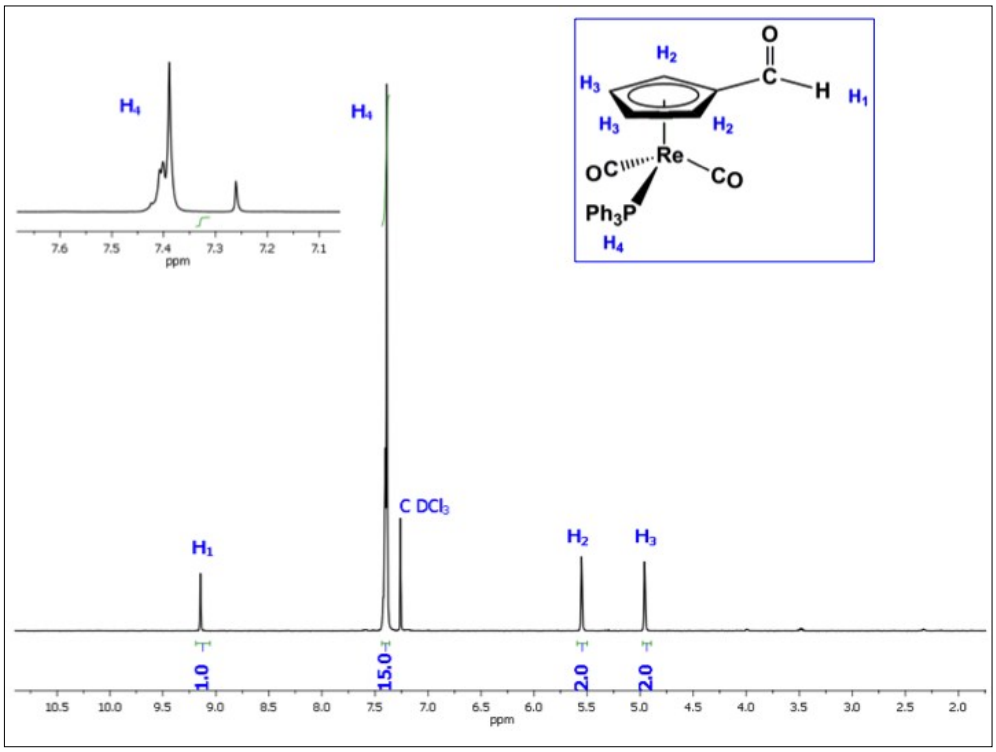

Figure S4. ^{1}H-NMR spectra (400 MHz) of a solution of **2b** (40 mM) in $CDCl_3$ at 298 K.

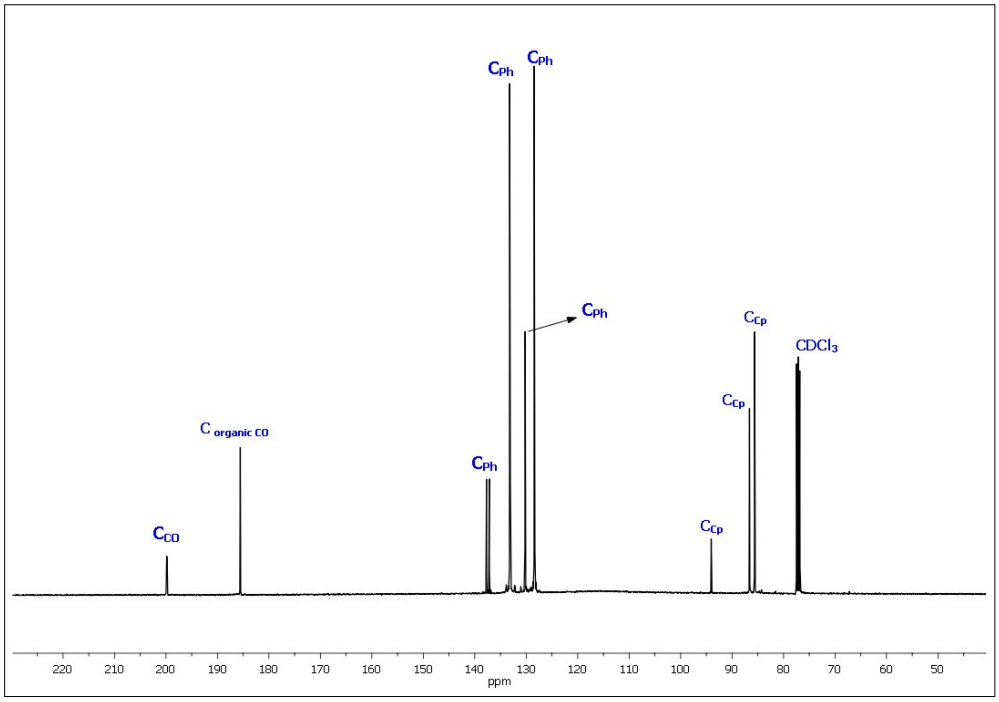

Figure S5. ^{13}C-NMR spectra (400 MHz) of a solution of **2b** (80 mM) in $CDCl_3$ at 298 K.

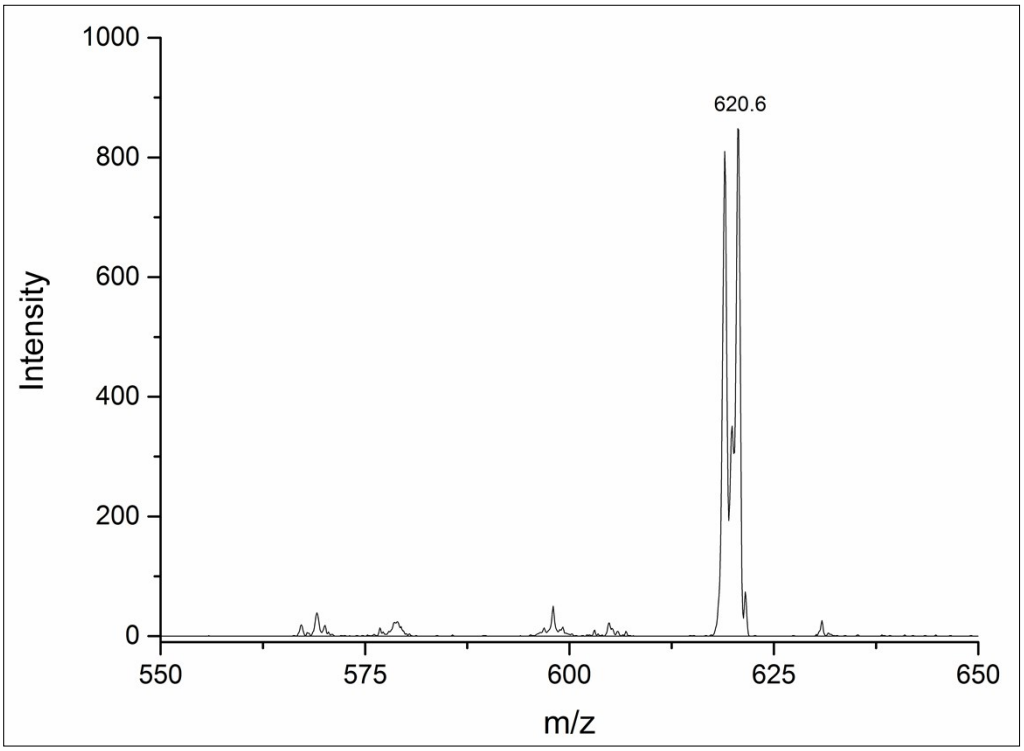

Figure S6. ESI-MS in CH_3CN of **2b** (1mg/ml).

a.3. Synthesis of [(η^5-C_5H_4CHO)Re(CO)$_2$PCy$_3$] (2c)

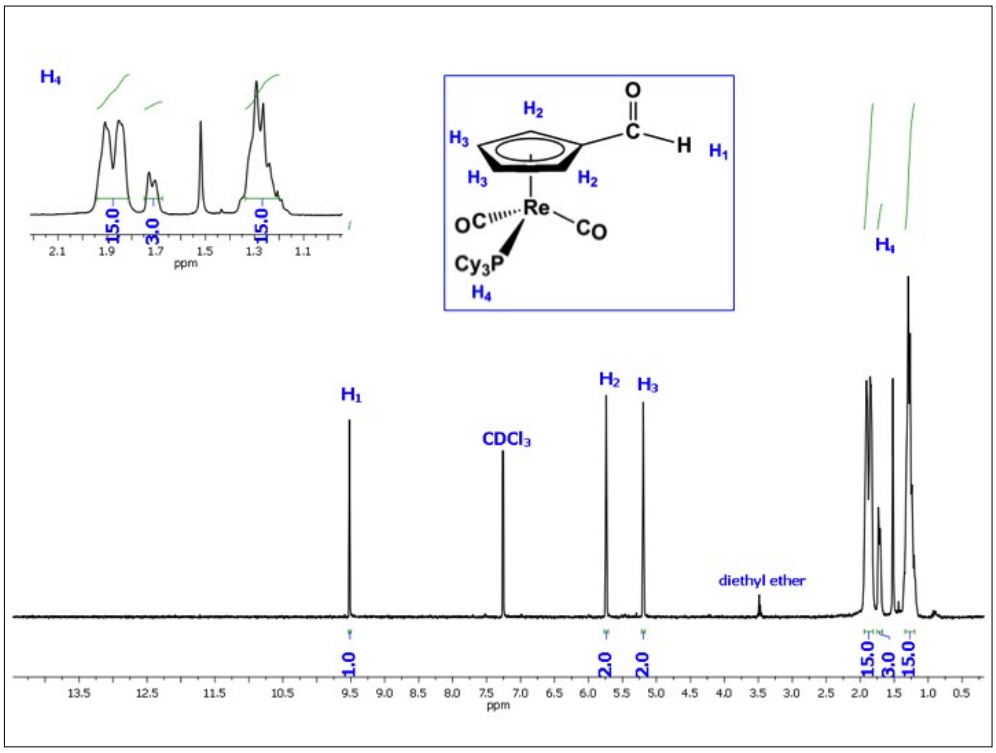

Figure S7. ^{1}H-NMR spectra (400 MHz) of a solution of **2c** (40 mM) in $CDCl_3$ at 298 K.

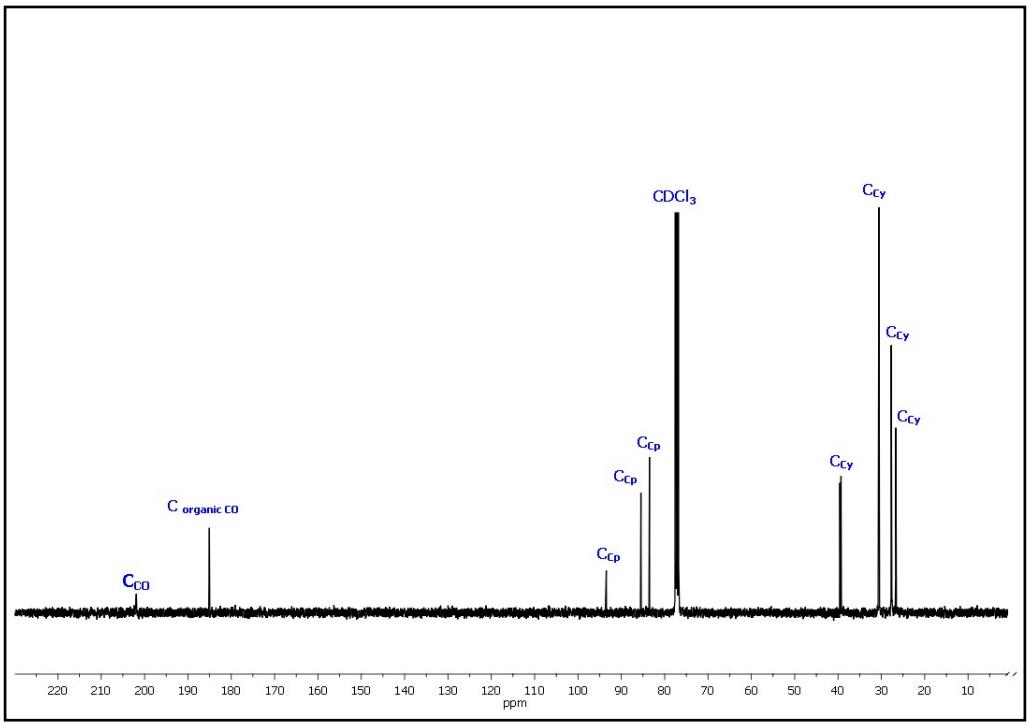

Figure S8. ^{13}C-NMR spectra (400 MHz) of a solution of **2c** (80 mM) in $CDCl_3$ at 298 K.

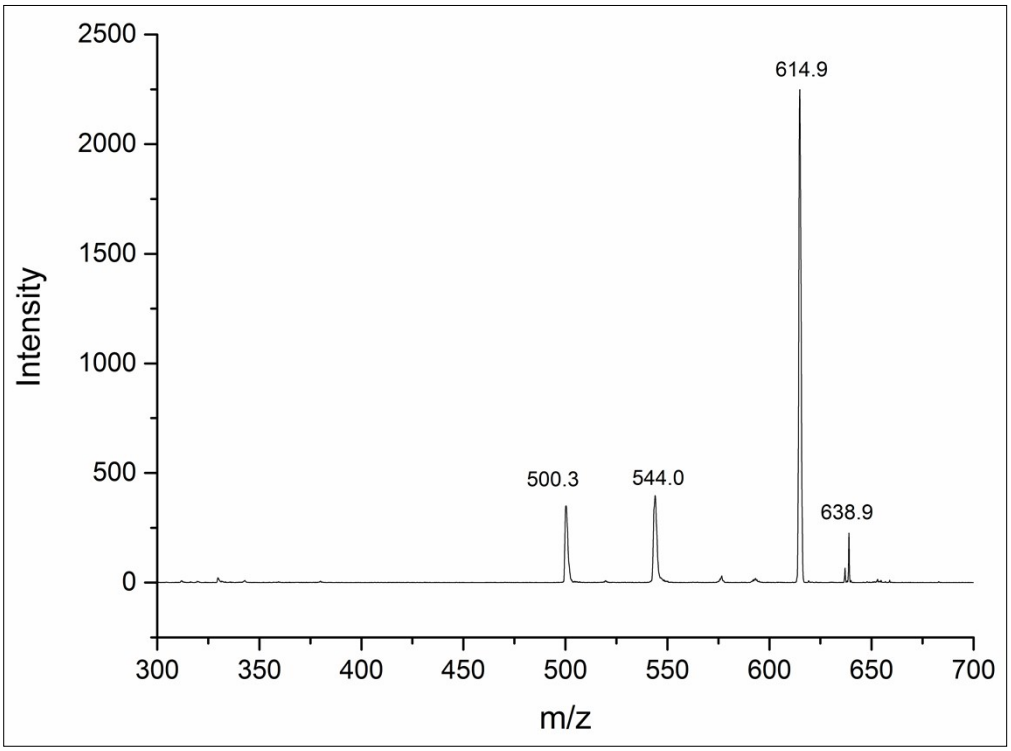

Figure S9. ESI-MS in CH_3CN of **2c** (1mg/ml).

b) Electrochemical studies

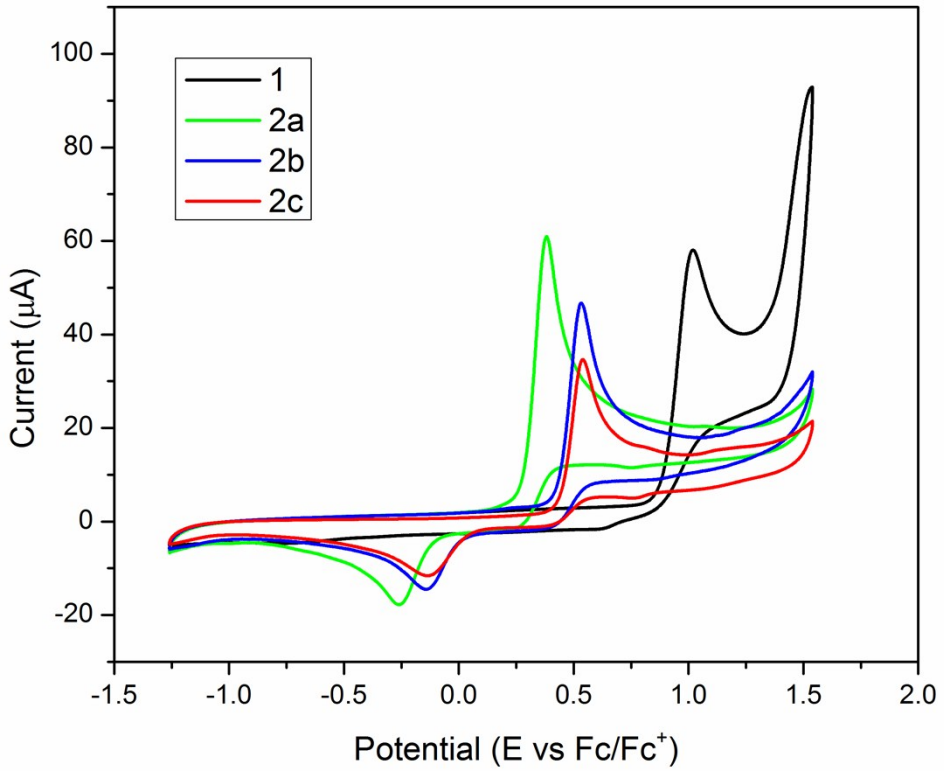

Figure S10. Cyclic voltammetry of phosphine derivatives **1** and **2a-c** (1mM), in dry CH_3CN using Bu_4NPF_6 (0.1 M) as the supporting electrolyte, at a scan rate of 100 mV/s.

c) Computational studies

Table S1: Experimental and calculated (DFT) frequencies υCO (cm^{-1}) of the symmetric and asymmetric stretching of the organometallic carbonyl ligand of each complex.

Compounds	Experimental	Calculated
1	2033, 1940	2048, 1944
2a	1935, 1867	1944, 1854
2b	1942, 1876	1957, 1872
2c	1928, 1860	1939, 1852

Table S2: Re-P distances from the DFT optimized structures

Compounds	Re-P (Å)
2a	2.36409
2b	2.36168
2c	2.40032

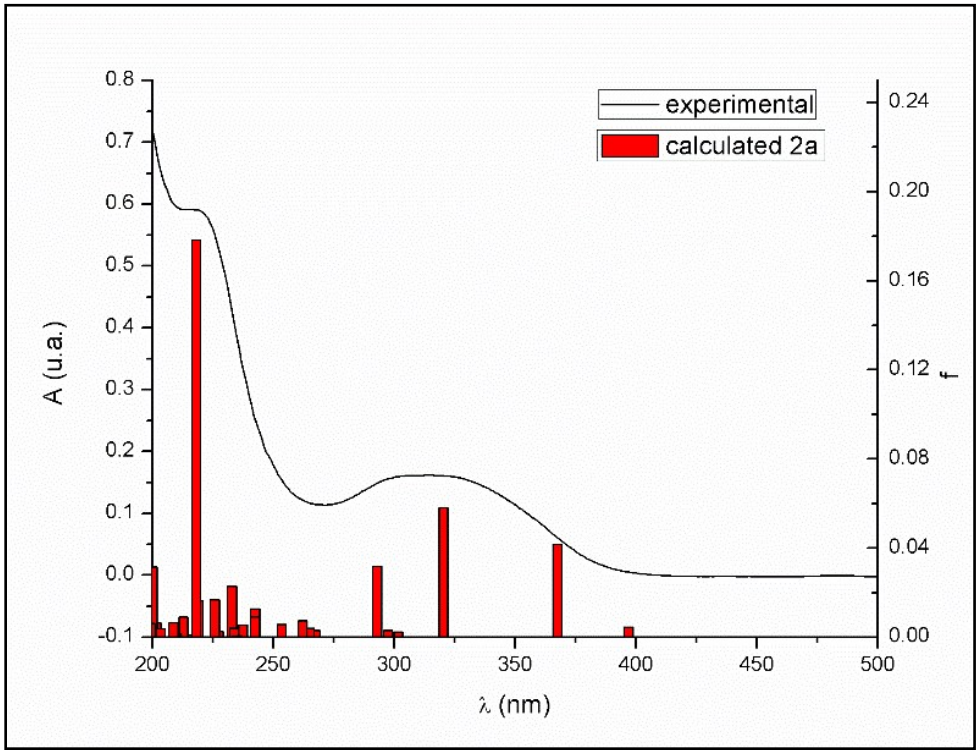

Figure S11. Experimental UV-Vis spectrum (black line) and electronic transitions (red bars) obtained for TD-DFT calculations of the complex **2a.**

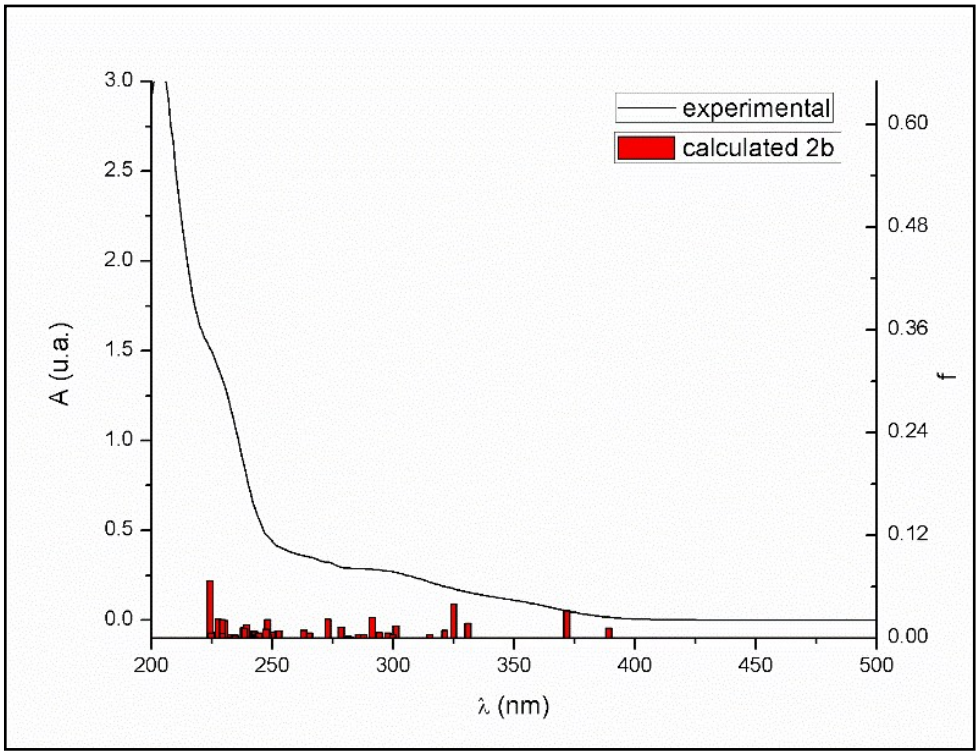

Figure S12. Experimental UV-Vis spectrum (black line) and electronic transitions (red bars) obtained for TD-DFT calculations of the complex **2b.**

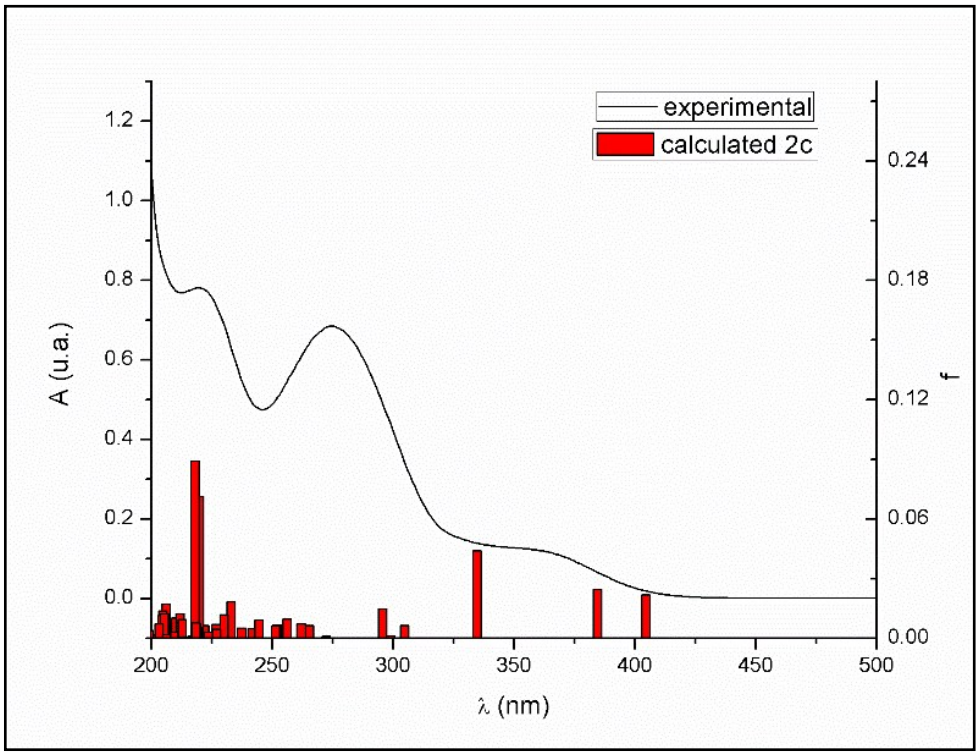

Figure S13. Experimental UV-Vis spectrum (black line) and electronic transitions (red bars) obtained for TD-DFT calculations of the complex **2c.**

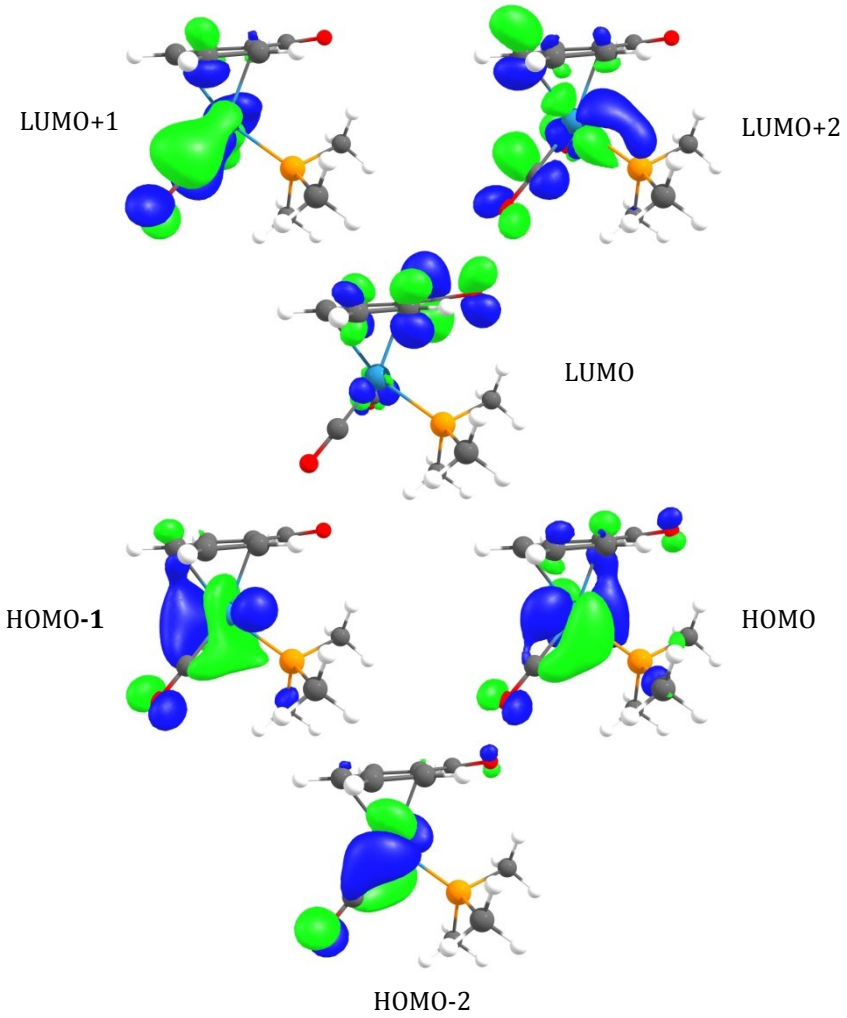

Figure S14. Calculated frontier orbitals of the complex **2a**.

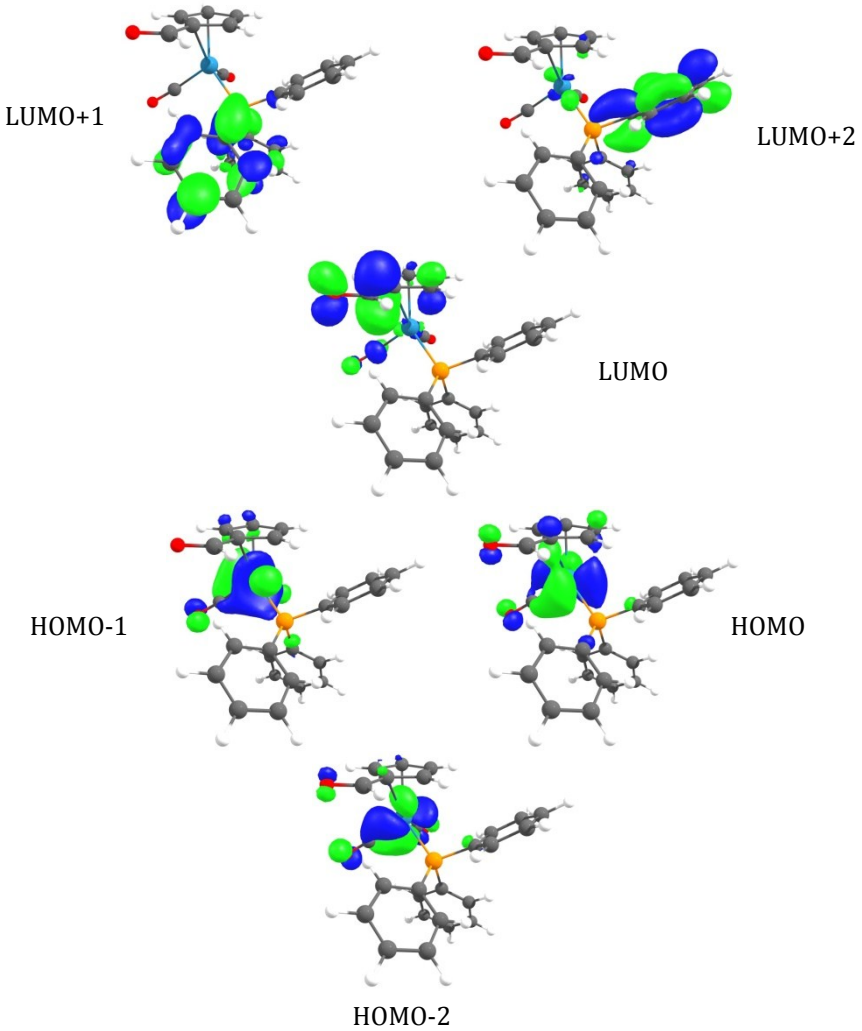

Figure S15. Calculated frontier orbitals of the complex **2b**.

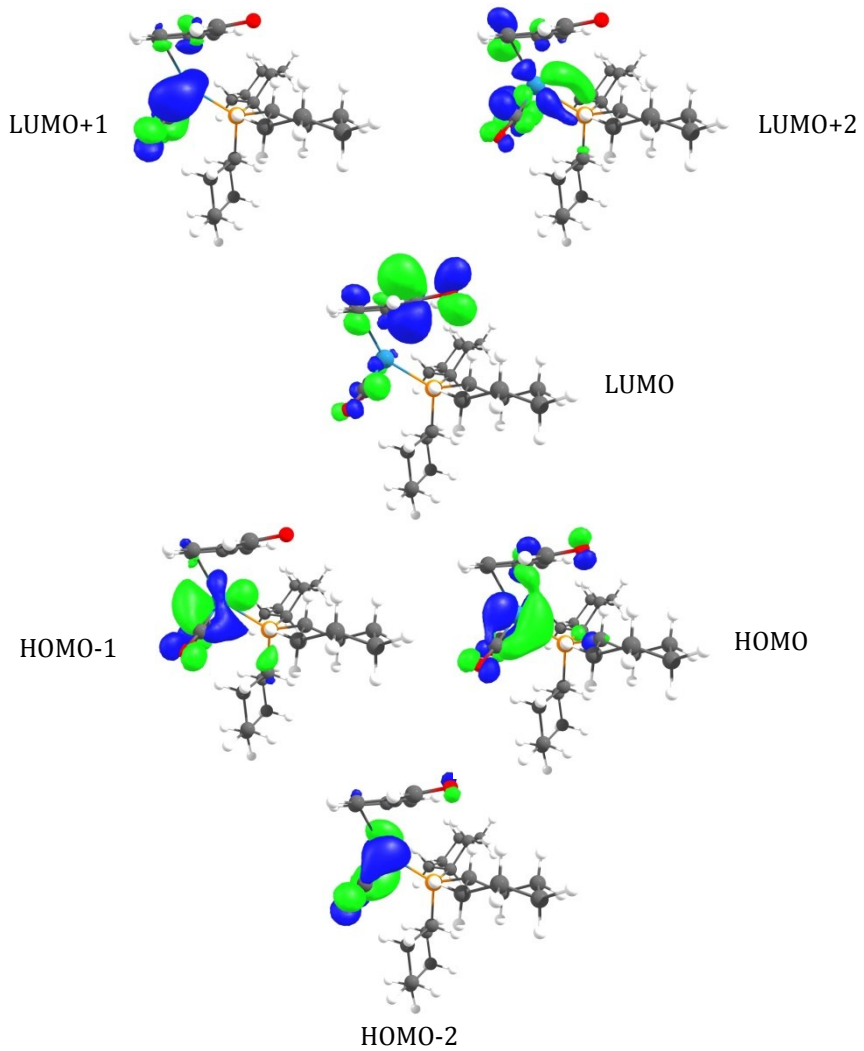

Figure S16. Calculated frontier orbitals of the complex **2c**.

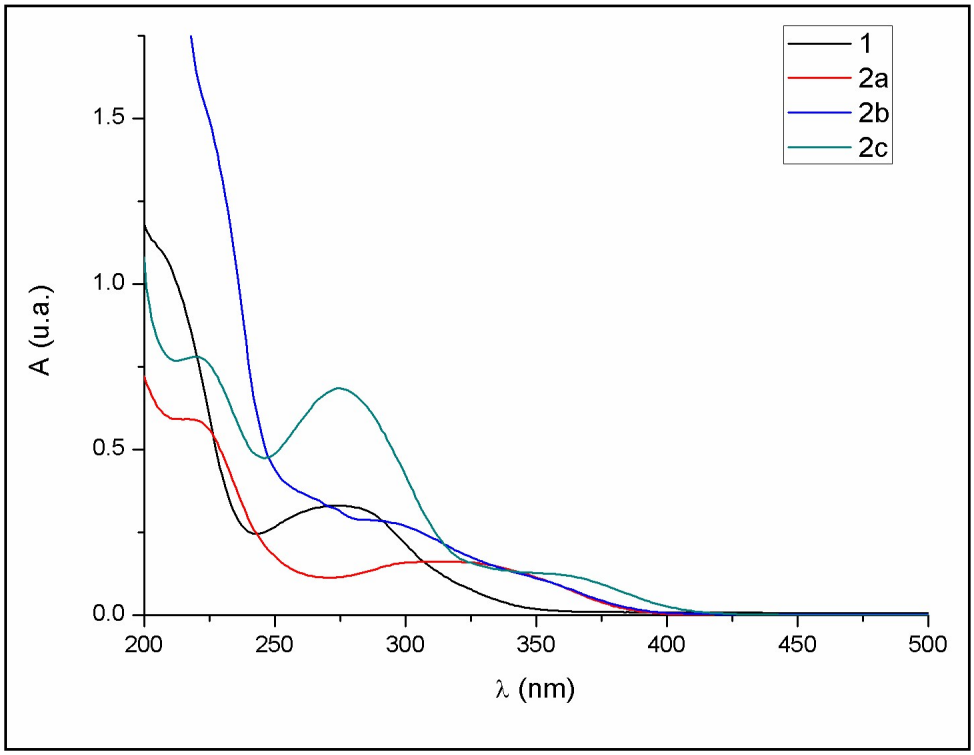

Figure S17. Experimental UV-Vis of 10^{-4} M solutions of **1**, **2a-c** complexes in CH_3CN at 298 K.

2. Cytotoxicity studies

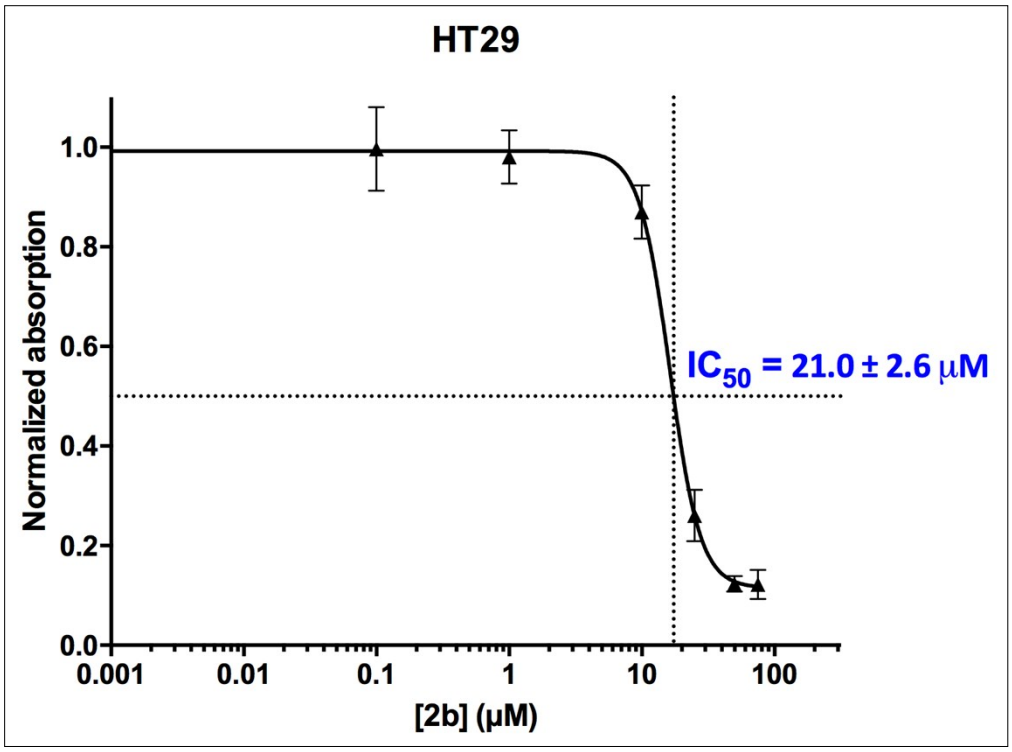

Figure S18. Biological Evaluation of **2b** in **HT-29**.

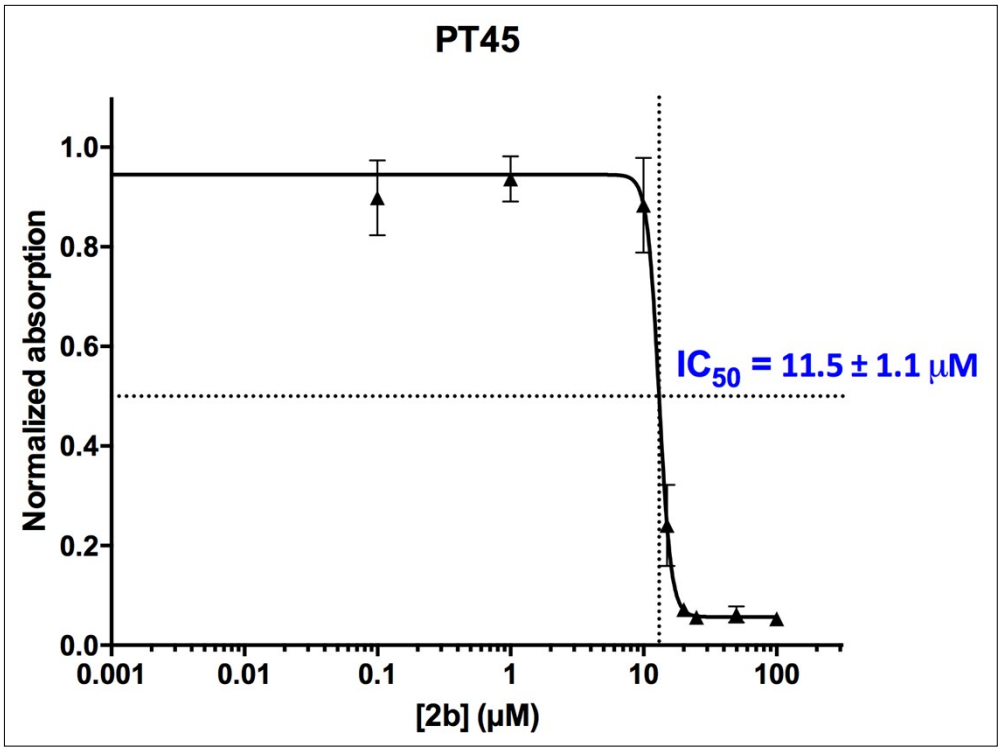

Figure S19. Biological Evaluation of **2b** in **PT-45**.